SINOMENINE AND DISINOMENINE. PART XXVIII. ON HOFMANN DECOMPOSITION OF DIHYDROSINOMENINE.

By **Kakuji GOTO** and **Hideo SHISHIDO.**

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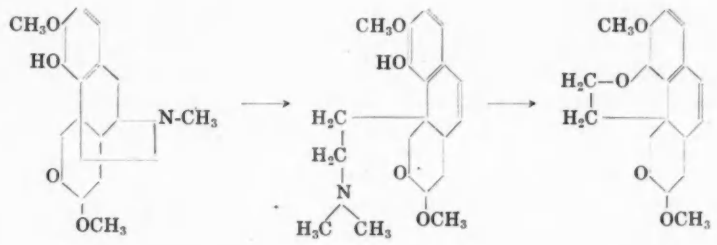
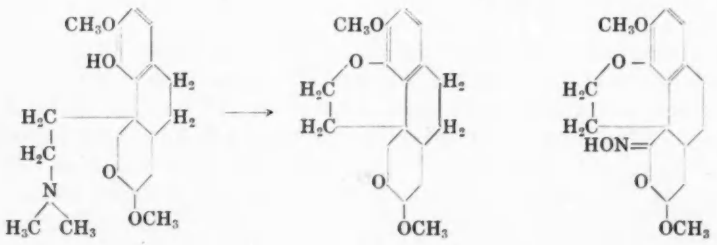
On Hofmann decomposition of sinomenine and its derivates, several communications have been published by us. In the present communication, dihydrosinomenine [I] was decomposed into the 7-methoxy-dehydro-*l*-thebenone [III] and into the 7-methoxy-*l*-thebenone [V] by the following process.



I. II. III.



IV. V. VI.

One remarkable feature in the above decomposition is that the sense of the optical rotation is inverted step by step from sinomenine to 7-methoxy-*l*-thebenone. The same phenomenon was observed in the *l*-thebenone and the *l*-thebenane series. As we have shown already, this inversion could be explained by the exalting action of the double bond only if we assume that

1. in sinomenine, $C_{(13)}$ is + and $C_{(14)}$ is −
2. the formation of an ether ring between OH in (4) and the side chain diminishes or inverts the rotatory power of $C_{(13)}$ or exalts that of $C_{(14)}$.

This hypothesis, which assumes $C_{(13)}$ to be + and $C_{(14)}$ to be − in sinomenine (hence $C_{(13)}$ to be − and $C_{(14)}$ to be + in morphine series) can be, however, applied only to the simplest cases such as the thebenone and thebenane series. In the three sinomenine methines, reported in the XXVth communication, this hypothesis is already faced with a grave difficulty. Of these three methines, sinomenine-violeo-methine seems to be most akin to the β- or δ-methylmorphi-methines, from the mode of its preparation and from its properties. But here it seems that the optical antagonisms between morphine and sinomenine series disappears or at least strongly diminishes. For, sinomenine-violeo-methine as well as its methyl-ether-methosulphate are strongly dextrorotatory (>300°) just like β- or δ-methyl-morphi-methines. This may be due partly to the fact that in morphine series there are two more asymmetric carbon atoms [$C_{(5)}$ and $C_{(6)}$] than in sinomenine. Yet, the ultimate reaction, we presume, must be sought in

(1) the influence of phenyl nucleus,
(2) the influence of the ring formation, viz. the nitrogenous ring, the ether ring and the hydrated third ring of the phenanthrene and
(3) the double linking,

as we have already mentioned.

The 7-methoxy-*l*-thebenone forms an isonitroso derivative by the action of amylnitrite and Na in ether. Although this isonitroso-derivative can not be obtained in a crystallised state, yet from the determination of N and methoxyl, it is clear that the isonitroso group must have been introduced in $C_{(5)}$. Then our assumption that the side-chain in sinomenine must be attached to $C_{(13)}$, made principally from its very easy splitting off, even by boiling 2% caustic soda in case of the sinomenine-violeo-methine, seems justly to have been added with a new proof.

Experimental

1. Dihydrosinomenine-methine [II]. Dihydrosinomenine iodomethylate (5 gr.) is boiled with 16.5% KOH (30 c.c.) for 70 minutes. The liquid is then diluted with water (30 c.c.), well cooled and saturated with CO_2, by

which the suspended oil drops crystallise out. The crystals are collected, washed with water and dried on a porous plate. Yield almost quantitative. Recrystallised from ether, it forms colourless long prisms. M.p. 173°C. (sintering at 160°C.).

Anal.: Subst. = 3.986; CO_2 = 10.140; H_2O = 2.806 mg. Subst. = 6.424 mg.; N_2 = 0.218 c.c. (12°C., 762 mm.). Found: C=69.38; H=7.82; N=4.02%. Calc. for $C_{20}H_{27}NO_4$ (345): C=69.56; H=7.82; N=4.06%.

Spec. Rotation. (0.2111 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)

$\alpha = -1.78°$ $[\alpha]_D^{18} = -84.32°$

2. 7-Methoxy-dehydro-*l*-thebenone [III]. Dihydro-sinomenine methine (6 gr.) was first turned into its iodomethylate by methyl iodide (6 gr.) in boiling methanol (30 c.c.). After the methyl iodide is perfectly evaporated off, the residue was decomposed by boiling 16.5% aqueous KOH (63 c.c.) for 35 minutes. The amine was caught in dilute HCl in this operation. The nitrogen free substance was then extracted with ether, after the free KOH was fixed with CO_2. It forms colourless prisms from ether. Yield 3.4 gr. M.p. 118°C. (Sinters at 113°C).

Anal.: Subst. = 5.989; CO_2 = 15.773; H_2O = 3.642 mg. Found: C = 71.83; H = 6.76%. Calc. for $C_{18}H_{20}O_4$ (300): C = 72.00; H = 6.67%.

Spec. Rotation. (0.2986 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)

$\alpha = -8.54$ $[\alpha]_D^{18} = -286.00°$

Oxime. 0.2 Gr. subst. was boiled in alcoholic solution (10 c.c.) with $NH_2OH \cdot HCl$ (0.4 gr.) and Na-acetate (0.4 gr.) for 2 hours. The crystals, deposited on evaporation of the alcohol, was well washed and recrystallised from alcohol. Prisms, which melt and decompose at 180°C.

Anal.: Subst. = 5.841 mg.; N = 0.213 c.c. (8°C., 760.4 mm.). Found: N = 4.38%. Calc. for $C_{18}H_{21}NO_4$ (315): N = 4.44%.

Nitrogenous substance. On evaporating the above hydrochloric acid, long needles of the hydrochloride of an amine was obtained, which was purified through absolute methanol. The chloro-aurate and the chloro-platinate melted at 246°C. and 249°C. respectively,

0.0907 Gr. chloro-aurate gave 0.0449 gr. Au. 0.0751 Gr. chloro-platinate gave 0.0278 gr. Pt. Found: Au=49.50; Pt=37.01%.

$[(CH_3)_3N \cdot HCl]\,AuCl_3$ and $[(CH_3)_3N \cdot HCl]_2\,Pt\,Cl_4$ require 49.37% Au and 36.97% Pt respectively.

3. Dihydrosinomenine-dihydro-methine [IV]. Dihydrosinomenine methine (2 gr.), dissolved in dilute HCl, was shaken in hydrogen atomosphere with $PdCl_2$ (0.1 gr.) and charcoal (1 gr.). The calculated quantity of hydrogen was absorbed in 5 minutes. The reduced methine was set free with Na_2CO_3 and extracted with ether, from which it separated out in prisms. M.p. 133°C. (sintering at 123°C.). Yield almost quantitative.

Anal.: Subst. = 3.586, 6.247; CO_2 = 9.08, 15.911; H_2O = 2.735, 4.633 mg. Subst. = 12.849 mg.; N_2 = 0.432 c.c. (12.1°C., 762 mm.). Found: C = 69.12, 69.46; H = 8.46, 8.24; N = 3.98%. Calc. for $C_{20}H_{29}NO_4$ (347): C = 69.16; H = 8.35; N = 4.03%.

Spec. Rotation: (0.4291 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)
$\alpha = +0.09$ $[\alpha]_D^{18} = +2.09°$

4. 7-Methoxy-*l*-thebenone [V]. (*A*) *From the dihydromethine* [*IV*]. Dihydrosinomenine dihydromethine (1 gr.) was turned first into its iodomethylate in the same way as described in (2). The iodomethylate, which was not crystalline, was decomposed by boiling with 16.5% aqueous KOH in the same manner as described in (2). The 7-methoxy-*l*-thebenone crystallised out from ether in glistening, colourless, long prisms. Yield 0.37 gr. (ca. 50%). M.p. 128°C. (sintering at 122°C.),

The nitrogenous substance showed the same properties as that obtained in the reaction (2) and was purified in the same way.

0.0430 Gr. the chloroaurate gave 0.0212 gr. Au. 0.0585 Gr. the chloroplatinate gave 0.0216 gr. Pt. Found: Au = 49.30; Pt. = 36.92%. Calc.: Au = 49.37; Pt. = 36.97%.

(*B*) *From 7-methoxy-dehydro-l-thebenone.* 7-Methoxy-dehydro-*l*-thebenone (2 gr.) was reduced catalytically in the same way as described in (3). The calculated quantity of hydrogen was absorbed in 30 minutes. The reduced substance crystallised out from ether in glistening prisms. M.p. 128°C. (sintering at 123°C.). Yield almost quantitative.

The mixed m.p. of the substances from (A) and (B) was unaltered. Anal.: Subst. = 4.780; CO_2 = 12.526; H_2O = 3.115 mg. Found: C = 71.46; H = 7.24%. Calc. for $C_{18}H_{22}O_4$ (302): C = 71.52; H = 7.28%.

Spec. Rotation. (0.2885 gr. Subst. in 10 c.c. chloroform, 1-dm. tube.)
$\alpha = -4.26$ $[\alpha]_D^{18} = -147.66°$

Oxime. Prepared quite in the same way as described in (2). Recrystallised from ethylacetate, it forms thick tetragonal plates. M.p. 168°C. (sinters at 145°C.)

Anal: Subst. = 8.739 mg.; N = 0.317 c.c. (11.2 °C, 761 mm.). Found: N = 4.31%: Calc. for $C_{18}H_{23}NO_4$(317): N = 4.41%.

5. Isonitroso-7-methoxy-*l*-thebenone [VI]. 7-Methoxy-*l*-thebenone (1 gr.) was dissolved in ether (50 c.c.) and ca. 1 gr. of natrium-wire was driven into it. To the ice-cooled solution, amyl nitrite (1.5 gr.) was added little by little. After standing overnight, the yellow precipitate at the bottom was collected on a glass filter and disolved in ice-water. By passing CO_2 in this solution, a resinous precipitate was formed, which was collected and dried in a vacuum-desiccator. The dried substance dissolved almost completely in ether, but showed no tendency to crystallise from it, or from ethyl alcohol. The analysis was carried out with the well dried substance.

Anal.: Subst. = 5.506 mg.; N = 0.199 cc. (18.5 °C., 758 mm.). Subst. = 9.197; AgI = 12.882 mg. Found: N = 4.13; CH_3O—(2) = 18.51%. Calc. for $C_{18}H_{21}NO_5$(331): N = 4.22; CH_3O—(2) = 18.73

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ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART IV.

NICKEL CYANIDE COMPLEX RADICAL.

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H. E. Williams[1] showed that nickel cyanide dissolved very readily in a solution of an alkaline cyanide, forming an orange-red solution of a double nickel cyanide of type, $M_2Ni(CN)_4$.

The following description is found in the book of analytical chemistry.[2] It produces an apple-green gelatinous precipitate by adding potassium cya-

(1) Cyanogen Compounds p. 66 (1915).
(2) Treadwell, Lehrbuch der analytishen Chemie, Vol. 1.

nide to a solution of a nickel salt, and this cyanide is soluble in excess of the reagent.

$$Ni^{++} + 2CN^{-} \rightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2CN^{-} \rightarrow Ni(CN)_4^{--}$$

Composition of Nickel Cyanide Ion. Nickel cyanide has been prepared by adding a solution of an alkaline cyanide to an excess of a nickel sulphate solution. In this case, author had an apple-green gelatinous precipitate of nickel cyanide, The precipitated nickel cyanide was purified by washing with conductivity water. Also nickel sulphate and nickel nitrate were purified by recrystallization. Then the ratio of combined cyanide to nickel in the complex ion was determined by a simple titration method.[1]

The results are summarized in the following tables.

Table 1.

Sodium Cyanide and Nickel Cyanide.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio of combined cyanide to nickel
0.1535	1.3308	0.6293	4.09
0.1456	1.3517	0.5926	4.07
0.1298	1.3922	0.5205	4.01
0.1195	1.4156	0.4765	3.98
0.1665	1.0109	0.6693	4.02
0.1372	1.0728	0.5488	4.00
0.1038	1.1344	0.4204	4.05
0.0988	1.1476	0.3972	4.03
0.0581	0.6363	0.2330	4.01
0.0390	0.6754	0.1556	3.99
0.0237	0.7064	0.0941	3.97
0.0165	0.7225	0.0635	3.85

Author obtained red colour solutions by adding pure nickel cyanide to 1.6531 and 1.3472 molal solutions of sodium cyanide, and also an orange colour solution by using 0.7530 molal solution of sodium cyanide.

(1) This Bulletin, **4** (1929), 190; ibid., **6** (1931), 60; ibid., **6** (1931), 89.

Table 2.

Sodium Cyanide and Nickel Sulphate.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0804	1.3295	0.3236	4.02
0.0662	1.3767	0.2764	4.17
0.0638	1.4001	0.2530	3.96
0.0578	1.4354	0.2177	3.78
0.0556	0.8000	0.2236	4.02
0.0519	0.8059	0.2177	4.19
0.0472	0.8295	0.1941	4.11
0.0444	0.8353	0.1883	4.24
0.0389	0.4471	0.1529	3.93
0.0352	0.4589	0.1411	4.00
0.0317	0.4706	0.1294	4.08
0.0289	0.4824	0.1176	4.06

Table 3.

Sodium Cyanide and Nickel Nitrate.

Nickel mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
0.0891	0.7269	0.3555	3.99
0.0731	0.7915	0.2909	3.98
0.0586	0.8488	0.2336	4.00
0.0549	0.8612	0.2212	4.03
0.0418	0.4544	0.1672	4.00
0.0379	0.4712	0.1524	4.02
0.0277	0.5124	0.1111	4.01
0.0212	0.5377	0.0859	4.05

In these cases of the Tables 2 and 3, author obtained red colour solutions by adding nickel sulphate or nitrate solution to the 1.0653 and 1.0824 molal sodium cyanide, and also orange colour solutions by adding nickel salts solutions to the 0.8000, 0.6000, and 0.6236 molal sodium cyanide solutions.

In all these experiments, the molal ratio of combined cyanide to nickel is four to one for all nickel salts, corresponding to the formula $Ni(CN)_4^{--}$. Hence it may be probably that the composition of the cyanide complex radical of nickel is $Ni(CN)_4^{--}$.

Stability of the Nickel Cyanide Ion. There is no available information on the concentration of nickel ion in nickel cyanide solution.

The potential differences between a nickel electrode and various solutions of nickel cyanide in sodium cyanide has been determined. The solutions used in these measurements were made by dissolving the appropriate amounts of pure nickel cyanide in 100 c.c. of 0.7852 mol NaCN solution. The electromotive force measurements were carried out at 25° C. by connecting a normal calomel electrode, through a normal KCl salt bridge, with an electrode of pure nickel wire immersed directly in the solution being constantly stirred. The obtained data are summarized in Table 4.

Table 4.

$Ni(CN)_4^{--}$	CN^-	E	E_w	Ni^{++}	K
0.06995	0.12511	0.7767	0.4946	4.92×10^{-10}	5.8×10^{13}
0.05316	0.14243	0.7863	0.5041	2.34×10^{-10}	5.6×10^{13}
0.02278	0.15591	0.7976	0.5154	7.33×10^{-11}	5.4×10^{13}

In Table 4, E is the measured electromotive force and E_w is the potential of the nickel electrode referred to the normal hydrogen electrode, taking the value of the single potential of the normal calomel electrode as -0.2822.[1] The nickel ion concentration was found by the equation.

$$E_w = E_o - 0.0295 \log c$$

where E_o is the standard electrode potential of nickel ion– nickel electrode and its value is 0.22 volt.[2] From the calculated value of (Ni^{++}), stability constant can be determined as follows:

$$K = \frac{Ni(CN)_4^{--}}{(Ni^{++})(CN^-)^4}$$

It will be noticed that K remains nearly constant in the Table 4. Therefore, we may conclude that in this case the complex ion is also $Ni(CN_4^{--})$.

Conclusion. The composition of the nickel cyanide complex ion is probably $Ni(CN)_4^{--}$ through all concentrations.

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(1) Lewis and Randall, Thermodynamics (1923), p. 407.
(2) Noyes and Sherrill, Chemical Principle (1920), p. 260.

ON THE OCCURRENCE OF A HYDROCARBON IN ISHINAGI LIVER OIL.

By Mitsumaru TSUJIMOTO.

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Of hydrocarbons occurring in the liver oils of animals, the most remarkable one is the highly unsaturated hydrocarbon, squalene, $C_{30}H_{50}$, which is contained in a fairly large number of shark liver oils, and although small in proportion, the saturated hydrocarbon, pristane, $C_{18}H_{38}$, usually accompanies squalene. In recent years, H. J. Channon and G. F. Marrian[1] found a hydrocarbon probably of the formula $C_{32}H_{54}$, $C_{33}H_{56}$ or $C_{34}H_{58}$, in the livers of man, sheep, horse, and pig; the present author in conjunction with K. Kimura[2] isolated a hydrocarbon, possibly corresponding to the formula $C_{35}H_{60}$, from the liver fat of sperm whale. However, so far as fish livers are concerned, no hydrocarbon has hitherto been discovered in them besides the above two hydrocarbons in shark liver oils. Recently I found a hydrocarbon in the liver oil of ishinagi, *Stereolepis ischinagi* (Hilgendorf). This oil, first investigated by me, is distinguished by the remarkable content of a vitamin A-like substance (liver resin), which sometimes amounts up to nearly 50% of the oil.[3] The amount of the hydrocarbon in the oil was small; it was highly unsaturated. Owing to the want of material, no definite formula has yet been assigned to it, but it appeared to be of a high molecular weight. The present paper is a preliminary report on this hydrocarbon.

Experimental Part.

The ishinagi liver oil used for the present investigation was a mixture of four samples of the oil prepared in the laboratory. It was a brownish red-yellow, viscous liquid, which appeared almost black in thick layer, and deposited an appreciable amount of solid fat in winter. An intense blue colouration was observed in the antimony trichloride test. The oil showed the following numbers:

d_4^{15}	0.9358	Saponif. value	146.2
n_D^{20}	1.5070	Iodine value (Hanus)	155.5
Acid value	11.8	Unsaponif. matter	22.36%

(1) *Biochem. J.*, **20** (1926), I, 409.
(2) *Chem. Umschau.*, **35** (1928), 317.
(3) Tsujimoto, *Chem. Umschau.*, **29** (1922), 385; S. Ueno, M. Yamashita and Y. Ôta, *J. Soc. Chem. Ind. Japan*, **31** (1928), 1198.

The fatty acids contained 68.5% of liquid acids, and consisted mainly of palmitic and oleic acids, together with stearic and clupanodonic acids. Hexadecenic acid and a small proportion of saturated acids higher than stearic were probably present.(1)

The unsaponifiable matter formed a reddish-orange, very viscous liquid. In order to separate the hydrocarbon, it was treated with methanol. 35 Gr. of the substance were heated with 350 c.c. of methanol, thereby complete solution occurred, but on cooling the solution became turbid, and an oily precipitate was gradually deposited. On standing over night, the supernatant liquid was decanted off; the precipitate was repeatedly washed with a small amount of methanol. In this way about 1 gr. of a yellow-orange, viscous liquid was obtained. It had an orange-yellow colour even after treatment with a pretty large amount of animal charcoal in ethereal solution. As the liquid was difficultly soluble in methanol, ethyl alcohol, and acetic anhydride, there was little doubt that it consisted mainly of hydrocarbon, but judging from its colour and colour reaction (Liebermann's), it appeared to be still impure. Owing to the difficulty of purification of such small material, it was analysed without further treatments as follows:

d_4^{17} 0.942 Iodine value (Hanus) 290.8

n_D^{17} ca. 1.54 ,, ,, (Rosenmund and Kuhnehenn) 310.0

Solidif. pt. Not solidified at 0°

Molecular weight. (1) 0.0114 gr. subst., 0.1307 gr. camphor (m.p. 177.7°), m.p. of the mixture 172°, depression 5.7°, mol. wt. 612. (2) 0.1442 gr. subst., 10.85 gr. benzol, depression 0.103°, mol. wt. 644.

Elementary analysis: Subst. = 0.1127; CO_2 = 0.3493; H_2O = 0.1187 gr. Found: C = 84.53; H = 11.79%.

Thus the substance had high specific gravity and refractive index, and as indicated by its iodine value, it was highly unsaturated. As the percentage of carbon and hydrogen amounted only to 96.32%, it was still impure to be taken as a hydrocarbon as had been anticipated.

Bromine addition compound. 0.1152 Gr. of the substance was dissolved in 10 c.c. of ether, and on cooling the flask with ice, a little excess of bromine was added. On standing for about one hour, the precipitate was collected on a filter and washed with ether; yield 0.1950 gr. or 169.3%. A white powder; on heating it became somewhat brown at 130°C., brown at 150°C., and turned black with sintering at 170°C. The bromine content was determined to be 67.07% (Carius).

(1) Tsujimoto, *Report of the Tokyo Imperial Industrial Laboratory*, Vol. **24** (1929), No. 4, p. 1.

Hydrogen chloride addition compound. 0.3 Gr. of the substance (not treated with animal charcoal) was dissolved in 10 c.c. of ether, and on well cooling, dry hydrogen chloride gas was passed into it to saturation. The solution showed various change of colour, and finally turned blackish violet. On standing for two hours, the precipitate was collected and washed with ether; yield 0.15 gr. On recrystallising it from acetone, a nearly white powdery substance was obtained. This sintered at above 120° C., and melted at 128–129°C. with bubbling (decomposition). The chlorine content was 30.85%.

Discussion.

The results of the above experiments were yet insufficient to determine the composition of the hydrocarbon. It was even questionable whether the substance consisted of a single compound. But assuming it to be so, the following two suggestions are possible, the decision of which I should postpone to further investigation:

(1) By assuming the high values of specific gravity, refractive index, and molecular weight to be due to some admixed impurities, and taking the halogen contents and the melting point of the comparatively pure bromine and hydrogen chloride addition compounds into consideration, it appears that the hydrocarbon closely resembles to that of the liver fat of sperm whale (loc. cit.), viz. Br content of $C_{35}H_{60}Br_{12}$=66.62%; Cl content of $C_{35}H_{60}6HCl$=30.42%.

(2) If we take the values of specific gravity, refractive index, and molecular weight to be nearly correct, then the substance is a compound higher than C_{40} atoms, and the number of double bonds must be more than six. The compounds nearly corresponding to these data are $C_{45}H_{76}$ (mol. wt. 616.6, iodine value 329.4 as eight double bonds) and $C_{46}H_{78}$ (mol. wt. 630.6, iodine value 322.1). The calculated halogen contents of the addition compounds are as follows:

	(%)		Cl (%)
$C_{45}H_{76}Br_{16}$	67.47	$C_{45}H_{76}8HCl$	31.23
$C_{46}H_{78}Br_{16}$	66.97	$C_{46}H_{78}8HCl$	30.75

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REACTION BETWEEN TRIMETHYLTIN HYDROXIDE AND METHYLIODIDE.

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Some years ago[1] the author noticed that a beautiful crystalline compound forms when trimethyltin hydroxide and methyliodide are put together in an ethereal solution. Recently this subject was undertaken by Kraus and Bullard[2] by measuring the conductivity of the mixture of trimethyltin hydroxide and methyliodide in acetone solution. They assumed the increase of conductivity of the mixtures due to the formation of a salt having the formula, $((CH_3)_3SnOH)_2CH_3I$. This has lead my attention to further investigation of this reaction. The experimental results show that the crystalline compound is identical with the compound which was obtained by the reaction between trimethyltin hydroxide and trimethyltin iodide[3]. Therefore, the reaction may be formulated as follows:

$$(CH_3)_3SnOH + CH_3X \rightarrow (CH_3)_3SnX + CH_3OH$$
$$2(CH_3)_3SnOH + (CH_3)_3SnX \rightarrow ((CH_3)_3Sn)_3O\cdot X\cdot H_2O$$

Experimental.

Two molecular proportion of trimethyltin hydroxide and one molecular proportion of methyliodide in a large amount of ethyl ether were introduced into a round bottom flask and connected with reflux condenser and heated on a water bath for about three hours. The solution of the mixture was filtered through filter paper while it was hot. The clear solution was kept over night in open air. From this solution a beautiful prismatic compound crystallized out.

On analysis it appeared to be identical to the compound formed between trimethyltin hydroxide and trimethyltin iodide in benzene solution.

Anal: Subs. = 0.2144, 0.1998; AgI = 0.0771, 0.0718 gr. Found: I = 19.44, 19.43%. Calcd. for $C_9H_{29}O_2Sn_3I$: I = 19.46%.

Subs. = 0.3511; SnO_2 = 0.2442 gr. Found (Carius): Sn = 54.77%. Calcd. for $C_9H_{29}O_2Sn_3I$: Sn = 54.59%.

(1) T. Harada, Thesis, Clark University, Worcester, Mass., 1923.
(2) Kraus and Bullard, *J. Am. Chem. Soc.*, **52** (1930), 4057.
(3) Kraus and Harada, ibid., **47** (1925), 2416; Harada, this Bulletin, **2** (1927), 105.

The Conductance of the Compound: No special precautions were taken, since the purpose of measuring the conductance of the compound was to get a general idea of the composition of the compound. The specific conductances of 0.1 N and 0.0166 N solutions of the compound in water were found to be 7.43×10^{-4} and 1.51×10^{-4} respectively and 1.41×10^{-4} and 0.35×10^{-4} in ethyl alcohol respectively expressed as reciprocal ohms at 23°C.

The magnitude of the specific conductance in water is about five times larger than that in alcohol. In other words, the extension of the dissociation of the compound in alcohol is about one fifth lower than it is in water. The equivalent conductances of the compound in alcohol at the concentrations, therefore, are 14.1 and 21.0 respectively. The specific conductance decreases as dilution increases. However, the equivalent conductance increases with increasing dilution. Therefore, the compound appears to be a salt.

Summary.

The reaction between trimethyltin hydroxide and methyliodide was studied. The compound formed from the mixture was identical to the compound formed from trimethyltin hydroxide and trimethyltin iodide having the formula $((CH_3)_3Sn)_3OX, H_2O$.

The conductance of the compound was studied. The results indicate that the compound appears to be a salt.

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THE CATALYTIC HYDROGENATION OF AROMATIC HYDROCARBONS UNDER HIGH PRESSURE AND HIGH TEMPERATURE.

By Ituo KAGEHIRA.

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Introduction

In connection with the hydrogenation of aromatic hydrocarbons, numerous methods have been suggested by Sabatier,[1] Ipatiew[2] and Schroeter,[3]

(1) Sabatier and Sendrens, *Compt. rend.*, **132** (1901), 1257.
(2) Ipatiew, *Ber.*, **40** (1907), 1281.
(3) Schroeter, *Ann.*, **426** (1922), 1

and their experimental studies indicate that the velocity of reduction is affected not only by the kind of catalyst employed and the pressure, but also by the chemical structure of the hydrocarbons. Very few investigators, however, have made a systematic survey of the relation between the catalytic reduction of aromatic hydrocarbons and their chemical constitution, and the present paper deals with this interesting problem.

Experimental.

The aromatic hydrocarbons which were used in the studies, were benzene, diphenyl, naphthalene, acenaphthene, anthracene, phenanthrene and pyrene, and they were all proved to be chemically pure except the phenanthrene, which contained a trace of a sulphur compound; their physical constants are shown in the table.

The reduced nickel used as a catalyst was made by heating nickel nitrate at about 300°C., and reducing it in a stream of hydrogen at 300°–320°C.; its activity was tested by its behaviour towards naphthalene.

Table 1.

Name	Appearance	d_4^{25}	n_D^{25}	B.P.	M.P.	Picrate	
						Appearance	M.P.
Benzene	Colourless liquid	0.8740	1.4972	—	—	—	—
Diphenyl	White thin plates	—	—	248–249 (756.5 mm.)	68.5–69.5	—	—
Naphthalene	White granular	—	—	212.5–213.5 (758.2 mm.)	80–81	Pale yellow needles	150–150.5
Acenaphthene	White needles	—	—	266.5–267.5 (760.2 mm.)	93–94	Orange-red needles	160.8–161.8
Anthracene	White thin plates	—	—	—	212.5-213.5	Red needles	139–140
Phenanthrene	White powder	—	—	—	98–100	Orange yellow thin plates	141–142
Pyrene	Yellow tetrahedral crystals	—	—	about 280° (757.5 mm.)	148–149	Red needles	222–223

In the experiments, a weighed sample was placed in an autoclave with freshly reduced nickel in the proportion of 8% of the weight of the sample, and after the air in the autoclave had been replaced by hydrogen, the gas was subjected to the required pressure, and heated externally by electric resistance to a definite temperature. During the reaction, the apparatus was shaken by a machine to bring the substance in contact with the hydro-

gen, and the change of temperature and pressure in the reaction chamber was recorded every 15 minutes. When the pressure became constant, the autoclave was cooled and the reaction products separated and fractionated by distillation, and purified by distillation or recrystallization. Their physical and chemical properties were then studied.

In the hydrogenation of benzene with 76 hydrogen atmospheric pressures at 0°C., the reaction started at 40°C and the reaction velocity at 200° C. to form hexahydrobenzene was found by calculation to be $\frac{96 \text{ gr.}}{315 \text{ minutes}} = 0.3$ (Fig. 1).

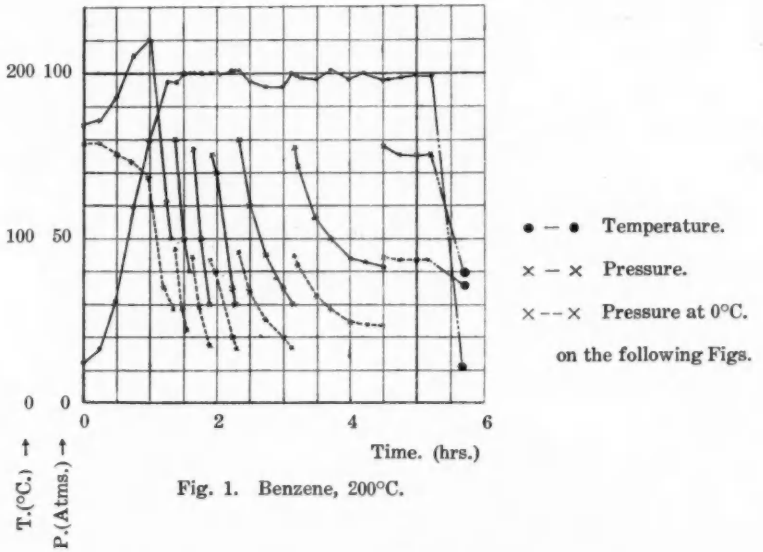


Fig. 1. Benzene, 200°C.

When diphenyl was hydrogenated catalytically with 95 hydrogen atmospheric pressures at 0°C., the initial temperature at which the reaction began was about 80°C., and dicyclohexyl was formed quantitatively at 200°C., the reaction velocity being $\frac{61}{225} = 0.27$ (Fig. 2). Hydrogenation at 250°C. and under 95 hydrogen atmospheric pressures at 0°C., however, resulted in the formation of phenyl cyclohexane, owing to the partial oxidation of dicyclohexyl formed directly from diphenyl (Fig. 3). Naphthalene on reduction at 200°C. and under 91 hydrogen atmospheric pressures at 0°C., yields tetrahydronaphthalene which is converted into a

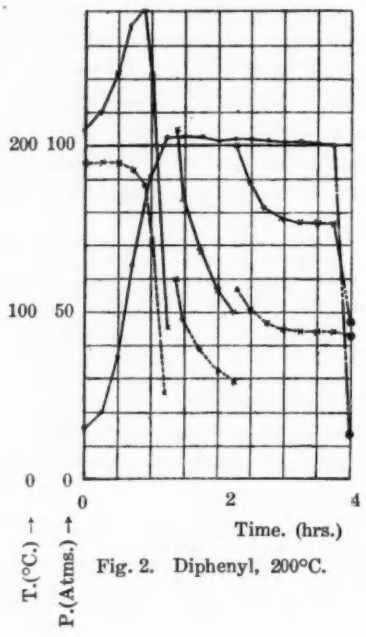


Fig. 2. Diphenyl, 200°C.

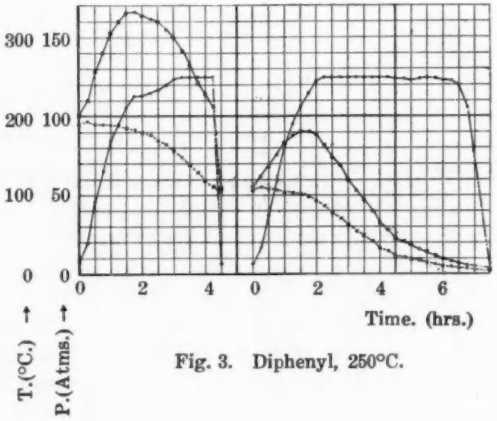


Fig. 3. Diphenyl, 250°C.

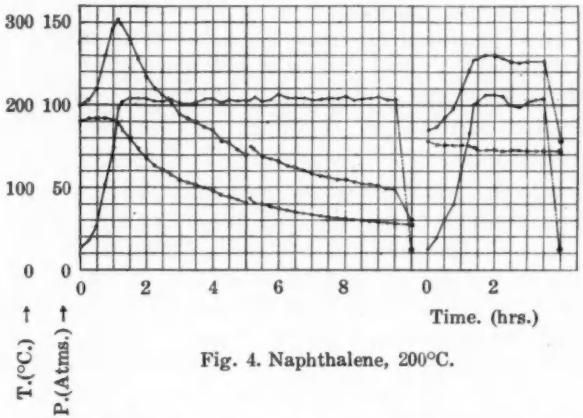


Fig. 4. Naphthalene, 200°C.

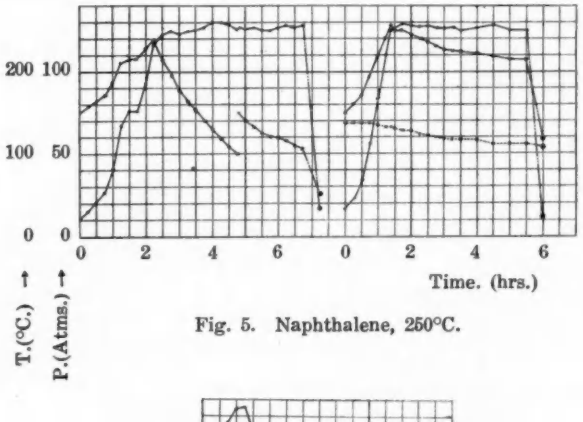


Fig. 5. Naphthalene, 250°C.

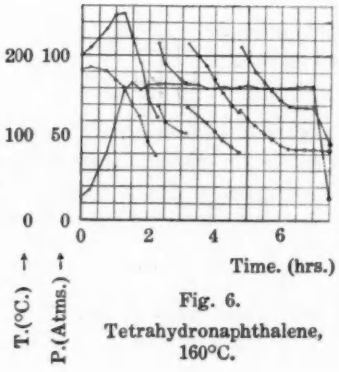


Fig. 6.
Tetrahydronaphthalene, 160°C.

decahydro-compound at 160°C. and under 91 atmospheric pressures. The hydrogenation of naphthalene seems to differ from that of tetrahydronaphtalene, the reaction in the former case having been observed to start with slow reaction velocity at about 140°C. under the conditions mentioned above, while that of tetrahydronaphthalene takes place at lower temperatures such as 80°C. (Figs. 4, 5, 6).

According to the principles of stereochemistry, there are two isomers in decahydronaphthalene, the cis- and trans-isomers, which have been studied by Mohr[1], Hückel[2], Willstätter[3], Eisenrohr[4], and Zelinsky[5]. The proportion of the cis- to the trans-isomer in the writer's sample was found to be 90 : 10, the calculation being made by the aid of the index of refraction and the specific gravity of the two isomers as observed by Willstätter and Hückel (See Table 2). The catalytic reduction of naphthalene at high pressure and high temperature seems to be similar, so far as the reaction product is concerned, to the case of the reaction of naphthalene with platinum and hydrogen at ordinary temperatures, but not the same as in Sabatier's method, in which the trans-isomer predominates in the reaction product.

Table 2.

	Decahydronaphthalene	
	Cis-form%	Trans-form %
Calc. from Willstätter's data		
of index of refraction	81	19
of specific gravity	97	3
Calc. from Hückel's data		
of index of refraction	62	38
of specific gravity	73	27

Acenaphthene on the other hand behaves quite differently from naphthalene in the catalytic reduction, though they show similar chemical structure; the absorption of hydrogen begins at about 80°C. under 94 atmospheric pressures at 0°C, and decahydroacenaphthene is produced at 200°C, the

(1) Mohr: *Ber.*, **55** (1922), 230.
(2) Hückel: *Ber.*, **58** (1925) 1449.
(3) Willstätter: *Ber.*, **56** (1923), 1388; **57** (1924), 683.
(4) Eisenrohr: *Ber.*, **57** (1924), 1639.
(5) Zelinsky: *Ber.*, **57** (1924), 2062.

reaction velocity being $\frac{103}{540} = 0.2$. The hydrogenation at higher temperatures (270°C.), however, produces tetrahydroacenaphthene due to the reverse reaction which occurs in the decahydro compound and which is favoured by higher temperatures (Fig. 7, 8).

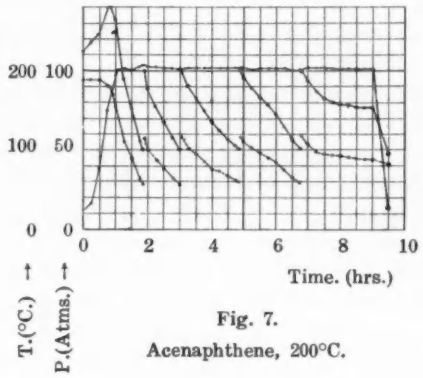


Fig. 7.
Acenaphthene, 200°C.

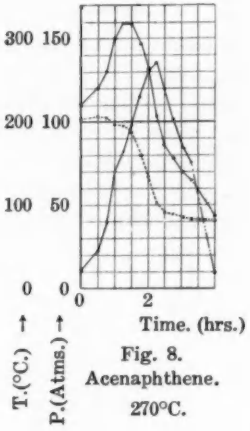


Fig. 8.
Acenaphthene.
270°C.

The reduction of anthracene is noteworthy in that the absorption of hydrogen begins at about 100°C. and the reaction by which the substance is converted into its octahydro-compound proceeds very quickly at 200°C., as was indicated by a fall of 30 atmospheric pressures in the pressure of the autoclave. Also, further reduction of the compound into perhydroanthracene will takes considerably longer time, as may be seen from Fig. 9.

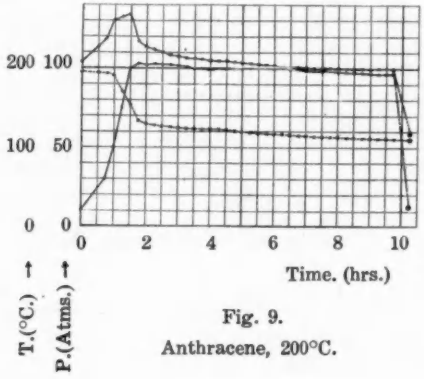


Fig. 9.
Anthracene, 200°C.

The reaction product consisted of three substances ; the first was in the form of colourless crystals melting at 72°C., (Found : C=90.5 ; H=10.5) identified with the octahydroanthracene obtained by Godchot[1] and Schroeter[2] ; the second, colourless crystals melting at 61°C., was proved to be perhydroanthracene by elementary analysis (Found : C=87.7 ; H=12.3) ; and the third, a liquid substance, was found by elementary analysis (Found : C=87.1 ; H=12.3) and by reference to its physical constants to be an isomeric substance with the perhydro-compound. The proportion of these substances in the reaction product was 1 : 3 : 2.

The fact that octahydroanthracene occurs with perhydro-compounds in the reaction product, indicates that two hydrogen atoms combined with carbon atoms, (9) and (10), in perhydroanthracene were removed on heating, as we experienced in the case of dihydroanthracene, resulting in octahydroanthracene as a reaction product.

(9)

(10)

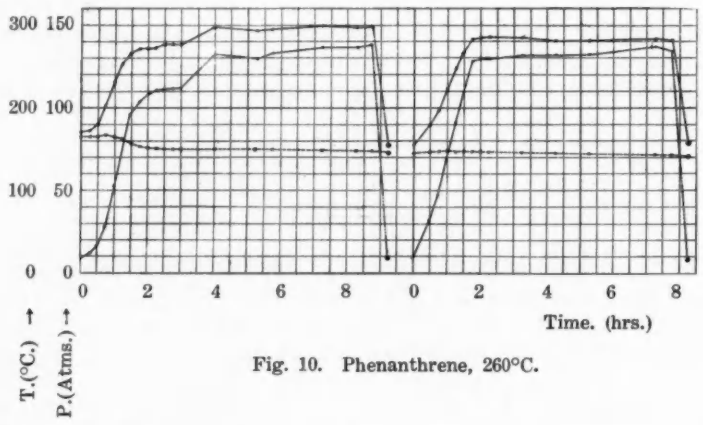


Fig. 10. Phenanthrene, 260°C.

(1) Godchot : *Ann. Chim.*, (8) **12** (1907), 1168.
(2) Schroeter : *Ber.*, **57** (1924), 2003.

In the reduction of phenanthrene, the reaction proceeded very slowly at 260°C. partly owing to the presence of some poisonous sulphur compound in it, and the product contained only 6% of tetrahydrophenanthrene (Fig. 10), which was separated from phenanthrene unchanged. The reduction was repeated with a new supply of hydrogen and reduced nickel, and octahydrophenanthrene was formed by heating at 175°C. for about 30 hours, which was identified from the physical properties. (Fig. 11).

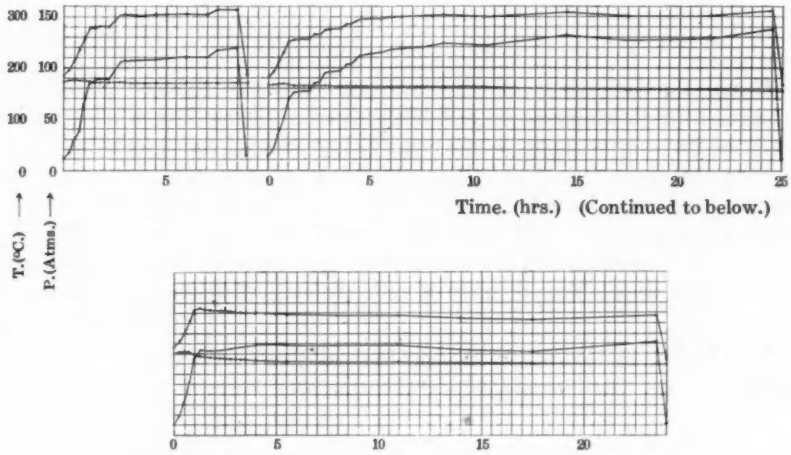


Fig. 11. Tetrahydrophenanthrene, 175°C.

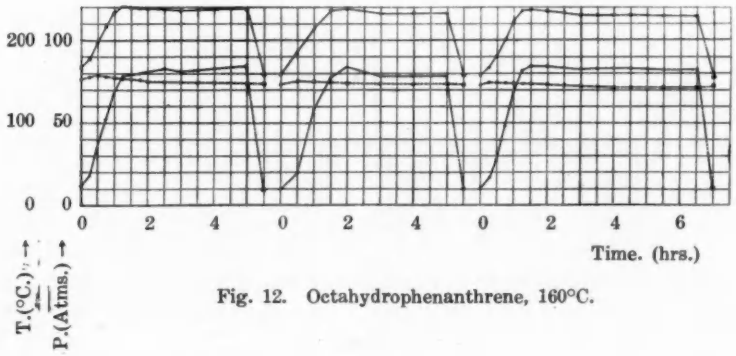
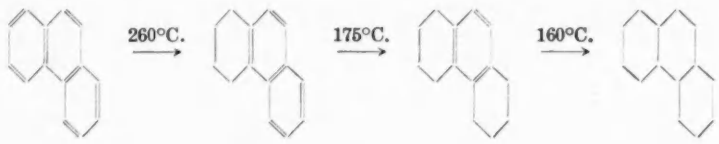


Fig. 12. Octahydrophenanthrene, 160°C.

To convert the octahydro-compound into perhydrophenanthrene, it was heated with hydrogen at about 160°C. for 5 hours under 77 atmospheric pressures at 0°C., and the yield of the pure compound was only 13% (Fig. 12). The catalytic reduction of phenanthrene may be represented by the following scheme :



Thus, the behaviour of phenanthrene towards reduced nickel and hydrogen at high temperature and high pressure, is, on the whole, similar to that of its isomeric anthracene, both being viewed as diphenylene compounds ; the group CH=CH in the phenanthrene molecule, by which two benzene rings are joined, is very difficult to keep in a reduced state at higher temperatures since these two carbon atoms, as we noticed in the oxidation of phenanthrene, are situated in a more reactive state than the other carbon atoms due to lack of uniformity in distribution of energy in the molecule.

The hydrogenation of pyrene was more difficult than that of the other hydrocarbons. The hexahydro-compound was formed with theoretical

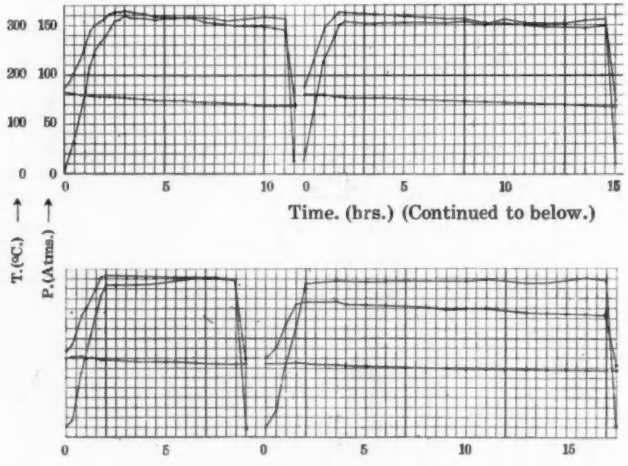


Fig. 13. Pyrene, 300°C.

yield when pyrene was heated with hydrogen at 300°C. for 52 hours under about 80 atmospheric pressures at 0°C. (Fig. 13); its physical properties, the results of elementary analysis (Found: C=92.2; H=7.7) and m.p. of picrate (118–119°C.) were identical with those of di-peri-di-trimethylene naphthalene obtained by Goldschmidt.[1]

Hexahydropyrene was regarded from the point of view of structure chemistry as a derivative of naphthalene or acenaphthene, and the catalytic reduction with reduced nickel and hydrogen at high temperature and pressure leads to a similar conclusion. When heated with hydrogen at 210°C. for 20 hours under 92 atmospheric pressures at 0°C., it yielded a substantial amount of decahydropyrene (Fig. 14), which was by further catalytic re-

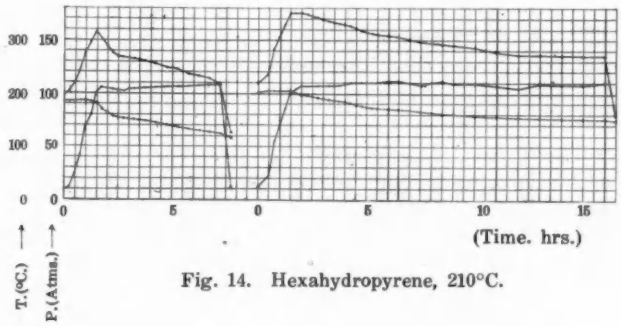


Fig. 14. Hexahydropyrene, 210°C.

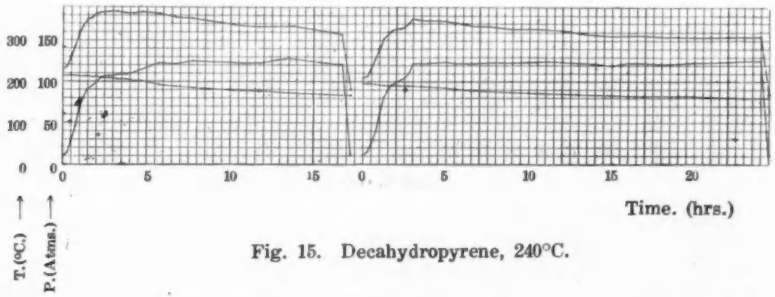


Fig. 15. Decahydropyrene, 240°C.

duction at 240°C. for 40 hours under 107 atmospheric pressures at 0°C., converted into perhydropyrene (Fig. 15). There are two isomeric forms of the perhydro-compound, the one consisting of colourless needles, m.p. 87–88°C., and the other being a liquid, b.p.=162–166°C. at 9.5 mm.; they were

(1) Goldschmidt: *Ann.*, **351** (1907), 218.

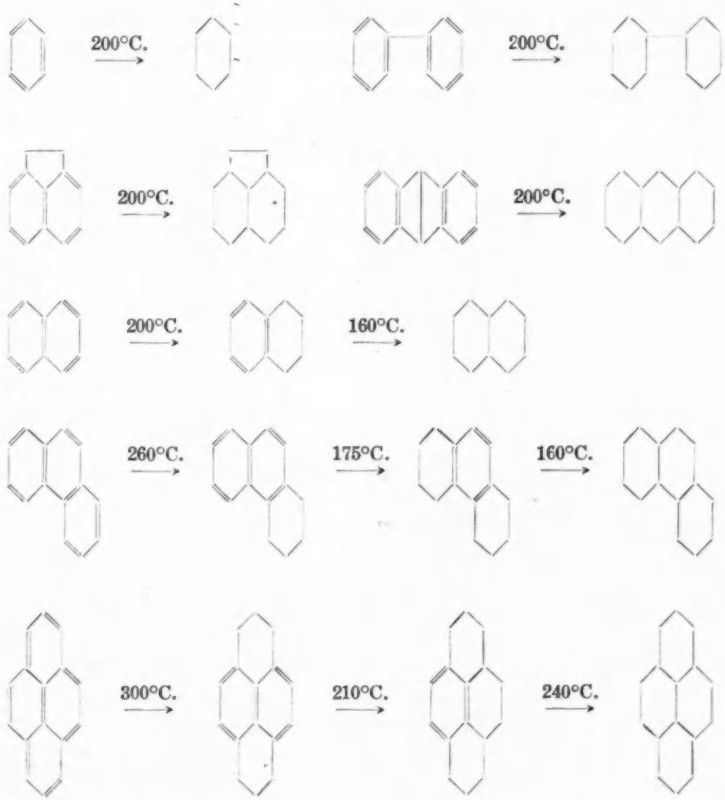
Table 3. The conditions and results of hydrogenation.

Number of experiment	Aromatic compound	Wt. (gr.)	Reaction temperature (°C)	Initial pressure at 0°C.	Hydrogen absorbed. atms. (obs.)	Hydrogen absorbed. atms. (calc.)	Time (hr.-min.)	Reaction product. Hydroaromatic compound	Yield (gr.)	d_4^{25}	n_D^{25}	M.R. obs.	M.R. calc.	B. P. (°C.)	M.P. (°C.)
7	Benzene	100	200	76	182	168	5–15	Hexahydrobenzene	96	0.7741	1.4235	27.69	27.70	80–80.5 (759.5 mm.)	
21	Diphenyl	65	„	95	115	98	3–45	Dicyclohexyl	61	0.8833	1.4772	53.20	53.22	231–233	
67	„	40	250	95	91	92	11–0	Phenylcyclohexane	37	0.9431	1.5313	52.56	51.82	234–236	
8	Naphthalene	100	200	91	71	67	13–0	Tetrahydronaphthalene	91	0.9675	1.5392	42.79	42.58	201.5–203.5	
9	„	„	250	69	74	67	12–15	Tetrahydronaphthalene	92	0.9678	1.5396	42.80	42.58	201.5–203.5	
18	Terahydronaphthalene	„	160	91	119	97	7–0	Decahydronaphthalene	97	0.8881	1.4753	43.82	43.87	189–191	
22	Acenaphthene	„	200	94	168	142	9–0	Decahydroacenaphthene	103	0.9488	1.4996	51.24	51.06	235–237	
66	„	„	270	102	62	57	3–20	Tetrahydroacenaphthene	96	1.0065	1.5550	50.42	49.62	245–248	
31	Anthracene	28	200	97	42	41	9–45	Octahydroanthracene	7					160–163 (13 mm.)	72–73
								Perhydroanthracene	14					150–155 (13 mm.)	60.5–61
								Perhydroanthracene	4.5	0.9747	1.5275	60.67	60.25	150–155 (13 mm.)	
33	Phenanthrene	100	260	83	13	42	16–30	Tetrahydrophenanthrene	7.2	1.0777	1.6322	58.96	57.92	170–180 (18 mm.)	
43	Tetrahydrophenanthrene	53	175	87	19	23	56–30	Perhydrophenanthrene	0.7	0.9630	1.5323	61.87	60.25	150–160 (18 mm.)	
								Octahydrophenanthrene	40	1.0232	1.5726	59.91	58.85	160–170 (18 mm.)	
44	Octahydrophenanthrene	15	160	77	3	9	16–30	Perhydrophenanthrene	2.0	0.9609	1.5261	61.41	60.25	155–165 (25 mm.)	
39	Pyrene	65	300	82	39	39	51–30	Hexahydropyrene	65						131–132
40	Hexahydropyrene	93	210	92	60	38	23–15	Decahydropyrene	89	1.0522	1.5713	66.28	65.89	196.5–201.5 (18 mm.)	
41	Decahydropyrene	70	240	107	40	40	40–45	Perhydropyrene	50						86.8–87.8
								Perhydropyrene	14	0.9828	1.5228	67.84	67.29	162–166 (9.5 mm.)	

proved to isomers so by elementary analysis (Found : C=87.9 ; H=12.1 for solid isomer and C=87.8 ; H=12.1 for the liquid) and also by their physical properties.

The method described above for the hydrogenation of aromatic hydrocarbons in the presence of reduced nickel under high pressure and at high temperature, has many advantages when applied to the synthesis of hydroaromatic compounds compared with the method of Sabatier or those proposed by Ipatiew and others, but in order to get the required hydrogenated compounds the reduction procedure shown in the table should be adhered to.

Table 4.



As will be seen in the above tables, aromatic hydrocarbons made up of two or more benzene rings, may be divided into two groups from the point of view of catalytic hydrogenation; the one can be hydrogenated completely by one experimental condition as we noticed in the case of benzene, but in the case of the other group to which naphthalene and phenanthrene belong, complete hydrogenation can be achieved only through two or more steps of reaction, with changes in the experimental conditions, especially in the reaction temperature.

In conclusion, the writer wishes to express his gratitude to Vice-Admiral G. Yamashita and Vice-Admiral S. Kishimoto, the former and the present Director respectively of the Imperial Naval Fuel Depot, and to Engineer Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch, for their kindness in enabling him to take part in this research, and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

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